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SOLID STATE

Increase in the Diamagnetic Response from Low-Density $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ High-Temperature Superconductors and $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ + Ag Composites

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Abstract—Low-density polycrystalline $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ high-temperature superconductors with a foamlike microstructure and composites consisting of this superconductor and silver in an amount of 20, 25, and 30 vol % are synthesized. The microstructure, as well as the temperature and field dependences of the magnetization, $M(T)$ and $M(H)$, are studied. It is found that, in $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ high-temperature superconductors and $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ + Ag composites, the diamagnetic response is enhanced and the screening properties are improved compared with high-temperature polycrystalline superconductors with the same composition that are prepared by the standard technology. The observed effect is explained by the features of magnetic flux penetration into a porous medium.

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For polycrystalline high-temperature superconductors (HTSCs) to be effectively used as a material for bearings, suspensions, magnetic screens, etc., it is necessary that the superconductor exhibit a high critical current density inside grains, since this parameter determines the levitation properties of the material. It is known that systems made of rare-earth-based HTSCs offer the best levitation properties [1]; however, this ceramics is prone to degradation as a result of hydrolysis, so that its application under the conditions of temperature cycling is limited. Under such conditions, bismuth-based HTSCs are preferable, because they are more stable and not liable to hydrolysis. At the same time, the levitation properties of bismuth-based polycrystalline HTSCs are much inferior to those of rare-earth-based HTSCs.

Earlier, we reported an increase in the diamagnetic response and pinning force in low-density $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ HTSC with a foamlike microstructure [2]. This material features open porosity, as a result of which liquid nitrogen readily penetrates into it, providing efficient heat removal from the interior of the sample under operating conditions. The I–V characteristics and the broadening of the resistive transition in porous $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ HTSCs in a magnetic field have been studied elsewhere [3, 4].

To see how porosity influences the amount of the diamagnetic response and shielding properties, in this work we studied the structure and magnetic properties of $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ HTSC samples with different physical densities and different volume concentrations of silver. Ultrafine silver particles added to an HTSC are known to create additional pinning centers and, consequently, improve the current-carrying capability of the material [5, 6]. Because of this, it seems reasonable to synthesize composites containing a low-density HTSC and silver and study their magnetic properties.

High-density polycrystalline HTSCs are synthesized by the standard ceramic technology [7]. To obtain low-density samples, we used the same technology but changed the conditions of final annealing so that HTSC crystallites grew mostly in the *ab* plane. Since crystallites in a polycrystal are oriented randomly, such growth causes the volume of the material to increase. One more change in the technology was that calcium carbonate was decomposed during final annealing. An overpressure of carbon dioxide also aided in increasing the sample volume [2].

Low-density $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ + (20, 25, or 30 vol %) Ag composites were synthesized by the technology described in [8]. The only modification was that a precursor consisting of $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_1Cu_3O_{10}$ + $CaCO_3$ (needed to provide a low density of samples) was mixed with silver powder in desired proportions and homogenized.

The volume percentage of silver in the composites was chosen below, roughly equal to, and above the threshold of percolation over the nonconducting component. The weight of the sample was calculated by the formula $M_S = \rho_{HTSC}(100 - n) + \rho_{Ag}n$, where $n = 20$, 25, or 30 vol %; $\rho_{HTSC} = 5.95$ g/cm^3, and $\rho_{Ag} = 10.5$ g/cm^3. A micrograph of initial ultrafine silver is shown in Fig. 1. The charge was compacted to form pellets 20 mm in diameter and 2–3 mm in height. The samples were sintered at 820°C for 400 h. The result was low-density composites (≈20% of the theoretical density without regard to silver) with a silver content of 20, 25, and 30 vol %. Table 1 lists the designations and densities of the samples used in this work.

The X-ray diffraction patterns taken of the polycrystalline and low-density $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ samples always contained reflections from the Bi2223 and Bi2212 phases. The Bi2223 : Bi2212 weight ratio was estimated from the intensities of the (002) reflections. For samples designated foam1 and foam2, $(I_{002}2212/I_{002}2223)100\% = 5\%$. Debye powder patterns taken of the HTSC + Ag composites contained reflections from the Bi2223 and Bi2212 phases (with the same weight ratio) and also those from Ag. The relative intensity of the Ag reflection grew in proportion to the volume content of Ag in the composite.

Figures 2a and 2b show electron micrographs taken from the cleavage surfaces of low-density HTSC samples foam1 and foam2, respectively, while the micrographs in Figs. 2c and 2d were taken from composite Ag20. All the micrographs taken of the low-density samples show that the material consists of platelike microcrystallites 10–20 μm wide and 1–2 μm thick. Because of the random orientation of $Bi_{1.8}Pb_{0.3}Sr_2Ca_2Cu_3O_x$ microcrystallites, the superconducting foam has a specific flakelike structure, which increases its volume. It is seen from Figs. 2a and 2b that samples foam1 and foam2 differ only in size of intergranular voids, which is embodied in their different physical densities. In Figs. 2c and 2d, the other component of the composite, silver, is distinctly observed. In the process of synthesis, silver, being initially in the form of ultra-fine-dispersed powder, coagulates to form spherical objects with typical size d = 10–20 μm. It is seen that the silver produces extra weak bonds in the low-density HTSC, which may, in our opinion, add to the current-carrying capability of the material.

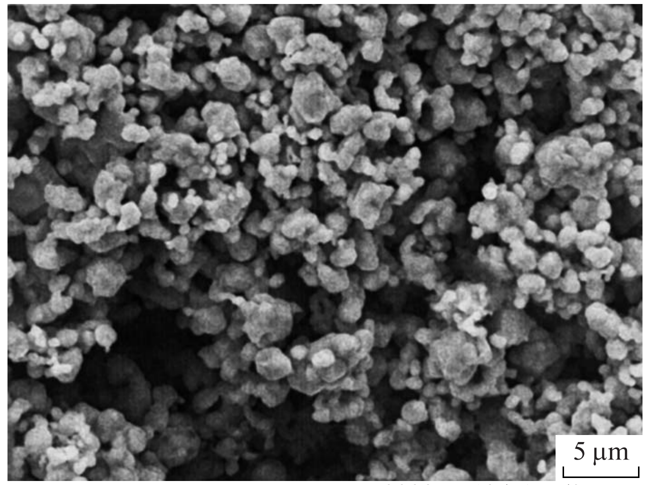

Fig. 1. Micrograph of initial ultrafine silver powder.

To reveal the effect of porosity and silver additive on the magnetic properties of the samples, we measured the temperature and field characteristics of the magnetization, $M(T)$ and $M(H)$. The magnetic properties were measured with a vibrating-sample magnetometer. The cylindrical samples were ≈0.5 mm in diameter and ≈5 mm long. The magnetic field was aligned with the axis of the cylinder. Curves $M(T)$ were taken under conditions of sample heating.

Figures 3 and 4 demonstrate magnetization hysteresis loops measured at liquid-helium and liquid-nitrogen temperatures, respectively. It is seen that the diamagnetic response from all the low-density samples increases in comparison with the standard polycrystalline one. Sample foam2 has the highest diamagnetic response: its remanent magnetization M_{rem} is 3.7 times higher than that of the standard polycrystal. The remanent magnetizations of all the samples are listed in Table 2.

For silver-containing composites Ag20, Ag25, and Ag30, the remanent magnetization per gram of the sample seems to be smaller than for pure porous sam-

Table 1. Density and designation of the samples

Sample	Density, g/cm^3	Percent of theoretical density	Designation
$Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$–polycrystal	5.72	95	poly
$Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$–foam1	2.26	38	foam1
$Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$–foam2	1.55	26	foam2
Composite 80 vol % $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ + 20 vol % Ag	1.19	20	Ag20
Composite 75 vol % $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ + 25 vol % Ag	1.19	20	Ag25
Composite 70 vol % $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ + 30 vol % Ag	1.19	20	Ag30

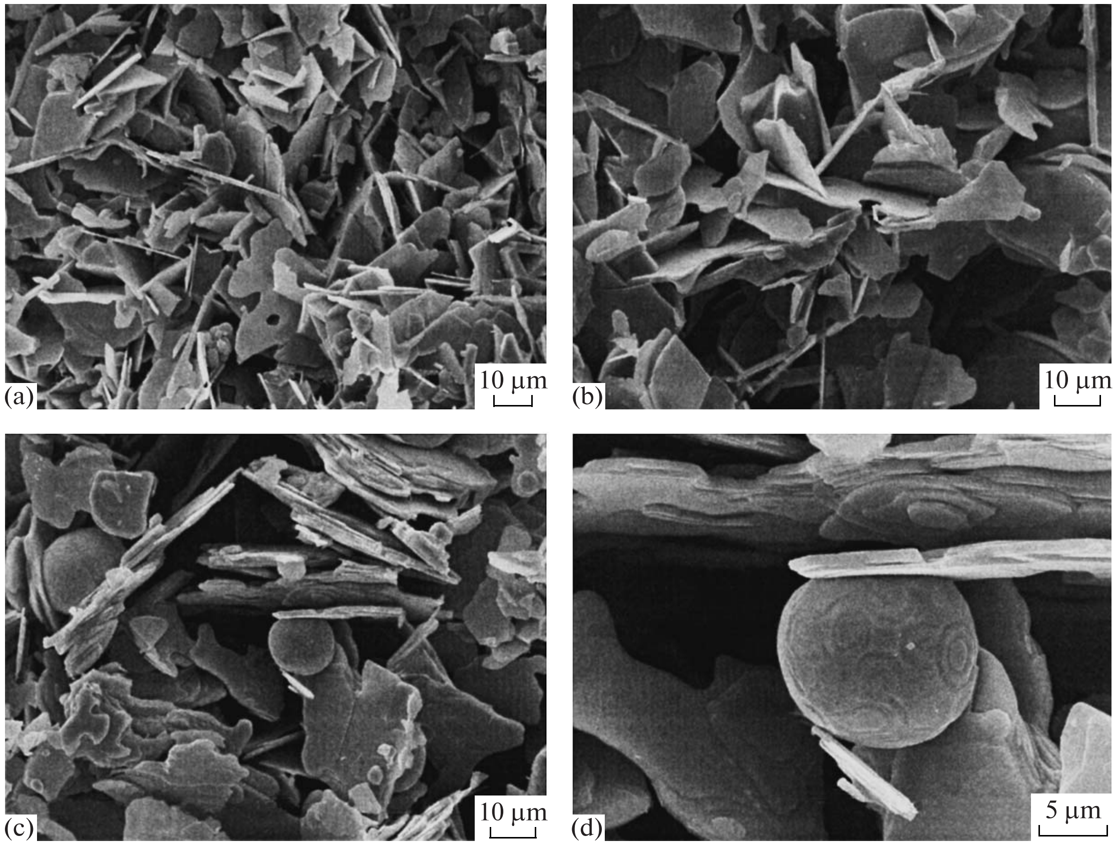

Fig. 2. SEM micrographs taken from natural cleavage surface of low-density HTSC samples (a) foam1 and (b) foam2.

ples. However, if the value of M_{rem} is converted with regard to the real weight of the HTSC in the composite (it is the HTSC that gives a diamagnetic response), it turns out to be close to M_{rem} of the pure porous ceramics. This indicates that the inclusions of ultrafine silver powder do not reduce the superconducting properties of the microcrystallites.

For complete characterization of the synthesized samples, we measured temperature curves of the magnetization, $M(T)$, at external magnetic field $H = 13$ Oe. It was found that superconducting transition temperature T_c, 108 K, is the same for all the samples. It is known that the difference between the magnetizations of the samples cooled in a magnetic field (field cooling), M_{fc}, and in the absence of a magnetic field (zero field cooling), M_{zfc}, is proportional to the pinning force and, hence, the critical current [9].

Figure 5 shows the curves $M(T)$ for the standard polycrystal and sample foam2. Both the maximal magnetization, $|M_{zfc}(77.4\text{ K})|$, and difference $\Delta M = |M_{zfc} - M_{fc}|$ are seen to be larger in the case of the low-density HTSC. This means that the pinning force and intragranular critical current in the low-density sample are higher.

The values of $|M_{zfc}(77.4\text{ K})|$ and difference $\Delta M = |M_{zfc} - M_{fc}|$ are listed in Table 3. For composites Ag20, Ag25, and Ag30, parameters $|M_{zfc}(77.4\text{ K})|$ and $\Delta M = |M_{zfc} - M_{fc}|$ are also higher than for the standard high-density polycrystal.

Thus, all the low-density samples studied in this work exhibit a diamagnetic response that is much higher than that of the high-density bismuth-based polycrystalline standard. Qualitatively, the reason for such an enhancement of the diamagnetic response may be the following. Since the superconducting foam samples contain open pores, the lines of magnetic force may penetrate into the sample at fields much lower than the first critical field, so that an external magnetic field is shielded by HTSC micro-

Table 2. Remanent magnetization of the samples at $T = 4.2$ K

Sample	$M_{rem}(H = 0)$, emu/g	$M_{rem}(H = 0)$, emu/g_{HTSC}
poly	9.83	9.83
foam1	25.44	25.44
foam2	36.58	36.58
Ag20	21.93	30.89
Ag25	15.58	24.75
Ag30	14.41	25.29

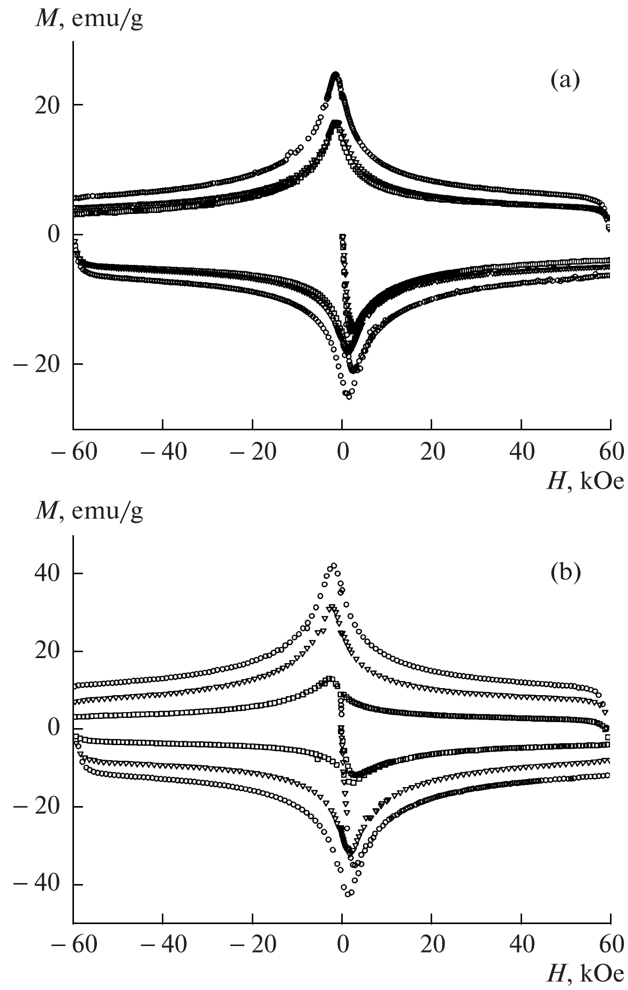

Fig. 3. Magnetization hysteresis loops $M(H)$ at $T = 4.2$ K for (a) composites (○) Ag20, (▽) Ag25, and (□) Ag30 and (b) HTSC samples (□) poly, (▽) foam1, and (○) foam2.

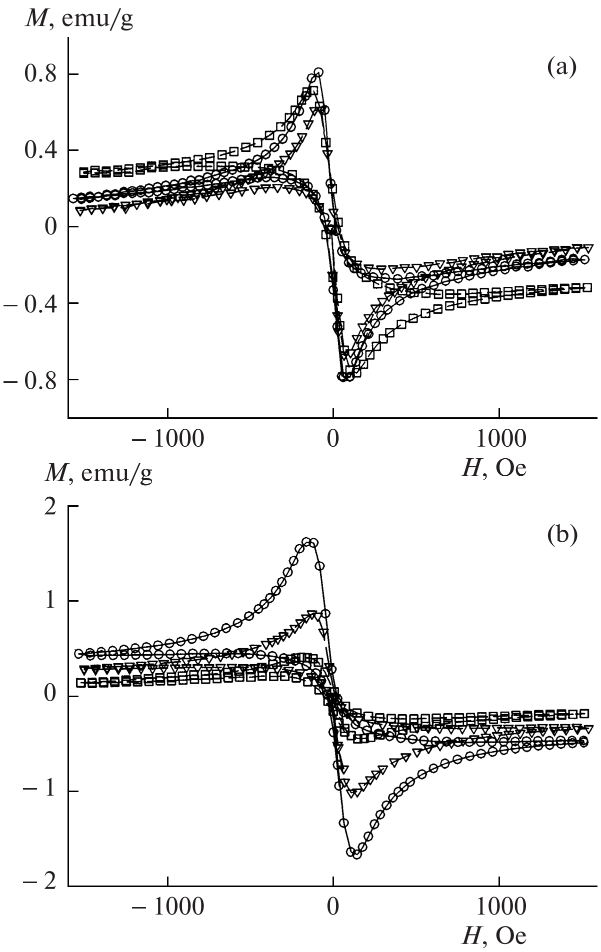

Fig. 4. Magnetization hysteresis loops $M(H)$ at $T = 77.4$ K for (a) composites (○) Ag20, (▽) Ag25, and (□) Ag30 and (b) HTSC samples (□) poly, (▽) foam1, and (○) foam2.

crystallites throughout the volume. Accordingly, the total magnetization of the sample is a sum of the magnetizations of individual crystallites. In the case of a high-density HTSC, an external magnetic field is shielded mostly by near-surface grains; that is, the volume of a high-density HTSC that participates in shielding is smaller than that of a low-density HTSC.

Table 3. Magnetic characteristics of the samples at 77.4 K

Sample	$\|M_{zfc}(77.4\text{ K})\|$, emu/g	$\Delta M = \|M_{zfc} - M_{fc}\|$, emu/g	$\|M_{zfc}(77.4\text{ K})\|$, emu/g$_{HTSC}$	$\Delta M = \|M_{zfc} - M_{fc}\|$, emu/g$_{HTSC}$
poly	0.066	0.018	0.066	0.018
foam1	0.188	0.086	0.188	0.086
foam2	0.267	0.129	0.267	0.129
Ag20	0.232	0.103	0.334	0.149
Ag25	0.173	0.093	0.275	0.148
Ag30	0.167	0.074	0.293	0.13

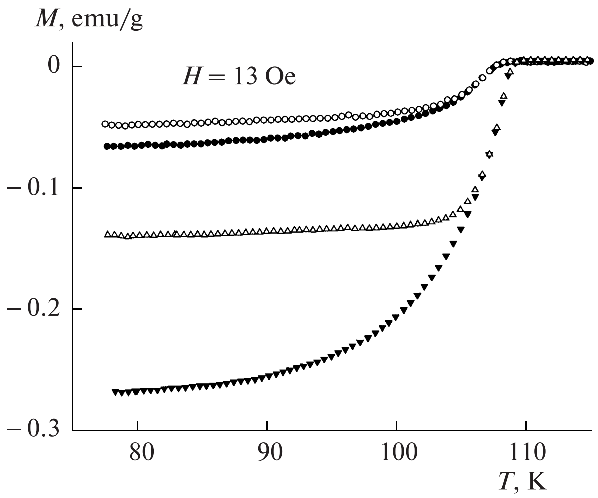

Fig. 5. Temperature dependences of the magnetization for HTSC samples poly (●, zfc; ○, fc) and foam2 (▼, zfc; △, fc).

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